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SMELTING REDUCTION OF IRON OXIDES FROM BAUXITE RESIDUE IN VIEW OF IMPROVED RARE EARTHS LEACHING

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Introduction

Bauxite residues that generated from karst bauxite ores are rich in REEs.[1] Direct acid leaching of REEs from bauxite residue yields low recovery rates, which can be improved by high acid concentrations but then high amounts of iron also dissolve.[2] Iron dissolution is not beneficial as it requires large amount of reagents during further ion exchange/solvent extraction processes.[3] Therefore, it is proposed to remove iron by smelting reduction and concentrate the REEs in the slag phase followed by acid leaching for recovery of REEs.[4]

Experimental

The bauxite residue used in this work was provided by the Aluminum of Greece. Chemical analysis of the material can be found elsewhere.[2] The bauxite residue sample was mixed with graphite powder (>99.5 wt.% purity) and wollastonite (51.2 wt.% CaO and 46.4 wt.% SiO_2) using a mortar and pestle. Handmade pellets were prepared from the mixture with addition of proper amount of water. The smelting reduction experiments were carried out in a high-temperature vertical alumina tube furnace (GERO furnace). The sample was heated to 1500–1600 °C in the presence of high purity argon at a heating rate of 5 °C/min and kept at the preset temperature for 1 h. The smelted samples were characterized with scanning electron microscopy (SEM, Philips XL30).

The slag sample was pulverized in a centrifugal mill (<80 μm). Small iron particles in the slag sample were removed by using a magnet after pulverizing. High-temperature leaching experiments were carried out in a 500-mL glass reactor fitted

with a reflux condenser and placed on a temperature-controlled ceramic hot plate with a magnetic stirring system. The leachate was filtered using a syringe filter (pore size of 0.45 µm) and diluted with 2 vol.% nitric acid aqueous solution for ICP-MS analysis.

Results and discussion

Smelting studies

The carbon requirement for iron oxide reduction was calculated based on the stoichiometric reaction (Equation 1).

$$Fe_2O_3 + 3C \leftrightarrows 2Fe + 3CO \quad (1)$$

The initial experiment was carried out with stoichiometric carbon (10 wt.% of the bauxite residue) and no flux at 1600 °C. No clear slag-metal separation was observed in the sample. Partial segregation of metal was observed at the bottom part of the sample due to the high density of the metal compared to that of the slag phase. SEM-EDX analysis of the sample showed that some silicon oxide and most of the titanium oxide were reduced to the metal phase. This is because of the residual carbon present in the sample due to the formation of CO_2 instead of CO below 900 °C. Therefore, further experiments were carried out with decreased graphite content. Flux (wollastonite) was added to decrease the slag melting point. Figure 1 shows the SEM images of the sample containing 20 wt.% wollastonite and 70% of the required stoichiometric carbon (7 wt.%) after smelting at 1500 °C. Wollastonite enhanced the metal separation but not up to the extent required. It was observed that the iron metal phase was locked by a titanium oxycarbide phase, which hinders iron separation. Therefore, the graphite content was further decreased. A clear slag-metal separation was now observed after smelting at 1500 °C with 20 wt. % wollastonite and 50% of stoichiometric carbon (5 wt.%), shown in Figure 2. No more iron oxides were observed in the slag phase. Therefore, 5 wt.% of graphite was chosen as the optimized amount. Subsequent experiments were conducted with varying amount of wollastonite i.e., 5, 10, 15, 20, 30 and 40 wt.%. Metal separation decreased drastically below 20 wt.% wollastonite. Clear slag-metal separation was observed above 20 wt.% of wollastonite. Therefore, 20 wt.% wollastonite was chosen as the optimized flux.

The iron nugget formed during smelting was easily separable from the slag. Around 85% of the iron was recovered in the form of this nugget. Small iron particles still in the slag phase were separated after grinding by using a hand magnet and amount to an additional 10% of iron.

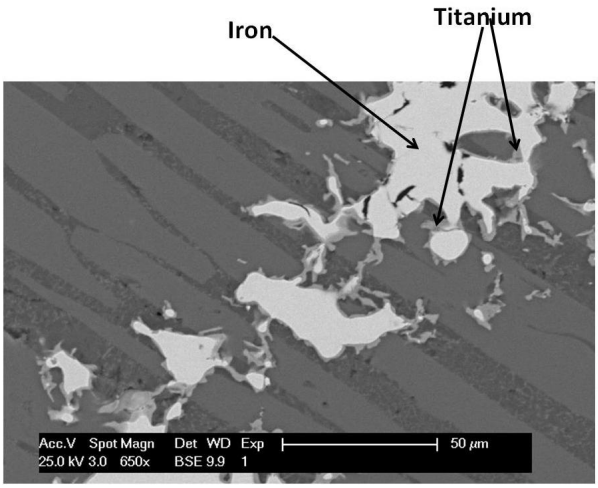

Figure 1. SEM image of the slag sample (20 wt.% wollastonite, 7 wt.% graphite, 1500 °C)

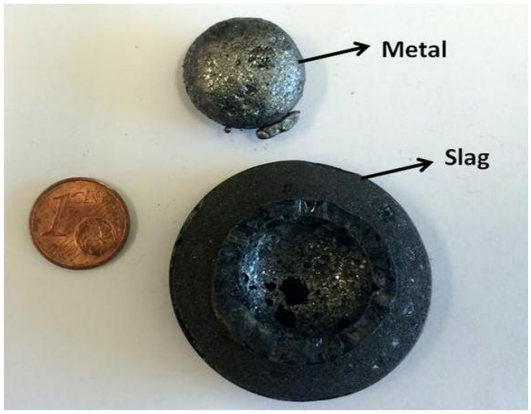

Figure 2: Image of the reduced sample (20 wt.% wollastonite, 5 wt.% graphite, 1500 °C)

Slag leaching studies

The chemical analysis of the resulting slag sample is given in Tables 1 and 2. The concentration of REEs in the slag was increased by a factor of 1.4 compared with that of the bauxite residue.

Table 1: Major chemical components in the slag sample

	Na_2O	Al_2O_3	SiO_2	CaO	TiO_2	Fe (total)
wt. %	2.18	33.54	24.45	28.13	6.83	1.31

Table 2: REE composition of the slag sample (g/tonne)

Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
166	120	173	577	41	155	30	6	35	4	27	5	18	2	18	2

Leaching experiments were conducted with HCl at 90 °C with liquid-to-solid (L/S) ratio of 50. The acid concentration was varied from 0.5 N to 3 N. The leaching results are shown in Figure 4. Results of bauxite residue leaching are also shown in the figure for the sake of comparison. The extraction of REEs increased with increasing acid concentration. The extraction is >90% for Sc and Y, >80% for Nd and Dy and >75% for La and Ce at 3 N HCl concentration. For ease of comparison, the iron dissolution from the slag shown in the figure is the percentage of the iron that is present in the bauxite residue. The extraction results of REEs from the slag are comparable with those from bauxite residue except for Sc at 0.5 N HCl, owing to the high pH (3.08) of the leach solution from the slag. It is difficult to leach REEs above 50-60% without dissolving a major part of the iron from the bauxite residue. However, most of the REEs can be extracted from the slag with only 4% of the Iron dissolution. Most of the Ca, Al and Na and around 70% of Ti from the slag are dissolved in 3 N HCl.

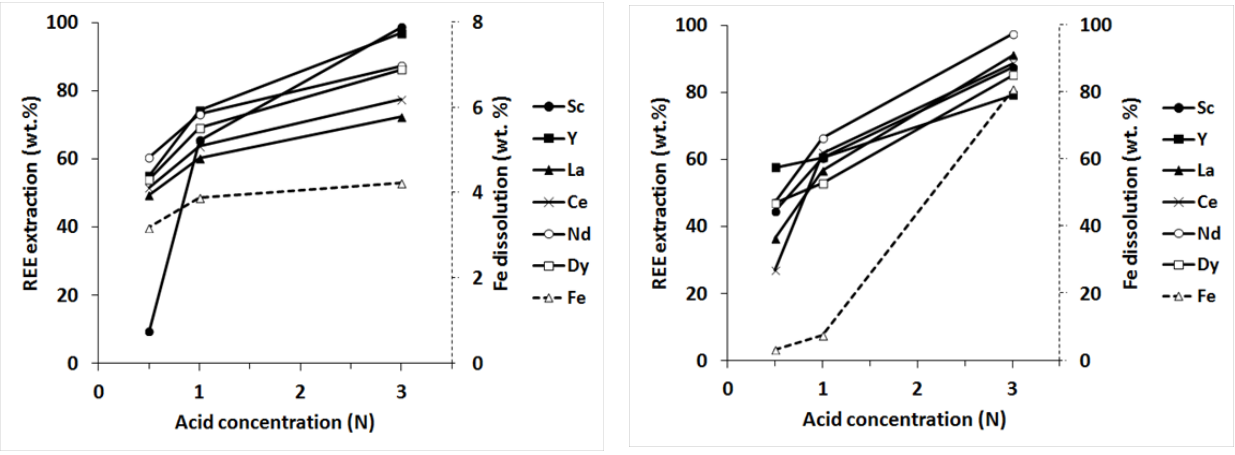

Figure 3: Effect of acid concentration on leaching of REEs and iron (HCl, T: 90 °C, t: 1 h, L/S: 50)

Conclusions

Iron from Greek bauxite residue was successfully removed in the form of nugget at 1500 °C by reductive smelting with 5 wt.% graphite and 20 wt.% wollastonite. A graphite content above 5 wt.% and wollastonite content below 20 wt.% decreased the slag metal separation. The main advantage of the slag leaching compared to bauxite residue leaching is that most of the REEs can be extracted with a low amount of iron dissolving into the solution.

Acknowledgements

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